We claim:

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A disaccharide selected from the group consisting of:

wherein

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or -OC(NH)CCl<sub>3</sub>;

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl.

- 2. The disaccharide of claim 1, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>.
- 3. The disaccharide of claim 1, wherein R' represents independently for each occurrence alkyl.
- 4. The disaccharide of claim 1, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 5. The disaccharide of claim 1, wherein said disaccharide is selected from the group consisting of:

TBSO O CO<sub>2</sub>Me NH Shoot OAc 
$$CCl_3$$
; and

A trisaccharide selected from the group consisting of:

wherein

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or -OC(NH)COl<sub>8</sub>;

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

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R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl

- 7. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>.
- 8. The trisaccharide of claim 6, wherein R' represents independently for each occurrence alkyl.
- 9. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 10. The trisaccharide of claim 6, wherein said trisaccharide is selected from the group consisting of:

$$\begin{array}{c} \text{MeO}_2\text{C} & \text{OBn} & \text{AcO} \\ \text{RO} & \text{BnO} & \text{O}_2\text{Me} \\ \text{AcO} & \text{BnO} & \text{O}_{\text{OLev}} \end{array}; \text{ and}$$

wherein

X is silyloxy or -OC(NH)CCl<sub>3</sub>; and

R is H or silyloxy.

A method of preparing a glycosaminoglycan, comprising the step of:

reacting a first mono-, di- or tri-saccharide, comprising an activated anomeric carbon, with a second mono-, di- or tri-saccharide, comprising a hydroxyl or amino group, to form an oligosaccharide, comprising a glycosidic linkage between said anomeric carbon of said first mono, di- or tri-saccharide and said hydroxyl or amino group of said second mono-, di- or tri-saccharide.

en C3

N

- 12. The method of claim 11, wherein the first mono-, di- or tri-saccharide is not identical to the second mono-, di- or tri-saccharide.
- 13. The method of claim 11, wherein neither the first mono-, di- or tri-saccharide nor the second mono-, di- or tri-saccharide is covalently linked to a solid support.
- 14. The method of claim 1), wherein the first first mono-, di- or tri-saccharide or the second mono-, di- or tri-saccharide is covalently linked to a solid support.

The method of claim 14, further comprising the step of:

cleaving said covalent linkage between said oligosaccharide and said solid support with an alkene metathesis catalyst and an alkene.

16. The method of Jaim 11, further comprising the step of:

sulfating a hydroxyl or amino moiety of said oligosaccharide.

17. The method of claim 11, further comprising the step of:

removing a hydroxyl or amino protecting group from said oligosaccharide by hydrogenolysis.

18. A method of preparing an oligosaccharide comprising an  $\alpha$ -glucosamine glycosidic linkage, comprising the step of:

reacting a uronic acid glycopyranosyl acceptor, comprising a hydroxyl group at C4 and a cyclic acetal comprising C1 and C2, with a glycosyl donor, comprising an activated anomeric carbon and an azide functional group at C2, to form an oligosaccharide comprising an  $\alpha$ -glycosidic linkage between said hydroxyl group of said uronic acid glycopyranosyl acceptor and said anomeric carbon of said glycosyl donor.

- 19. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is an iduronic acid glycopyranosyl acceptor.
- 20. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is a glucuronic acid glycopyranosyl acceptor.
- 21. The method of claim 18, 19, or 20, wherein said glycosyl donor is a glycosyl fluoride or glycosyl trichloroacetimidate.

22. The method of claim 21, wherein said cyclic acetal comprising C1 and C2 of said uronic acid glycopyranosyl acceptor is an isopropylidene acetal or a cyclopentylidene acetal.

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We claim:

(1.)

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A disaccharide selected from the group consisting of:

J. Carb. 14 Chem.
J. Carb. 14 Chem.
J. 295, 14 Chem.

; and

wherein

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or  $-OC(NH)CCl_3$ ;

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl.

- 2. The disaccharide of claim 1, wherein X represents fluoro, bromo, 4-pentenyloxy or -OC(NH)CCl<sub>3</sub>.
- 3. The disaccharide of claim 1, wherein R' represents independently for each occurrence alkyl.
- 4. The disaccharide of claim—1, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 5. The disaccharide of claim 1, wherein said disaccharide is selected from the group consisting of:

7: 1-4,6-9, 11-13,14,17

06f: 5, 10, 14, 15 18-22 free 4 p. 20t.

- 110 -

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or -OC(NH)CCl<sub>3</sub>; **7** 

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl. My one  $R^{1}$ 

- 7. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>.
- 8. The trisaccharide of claim 6, wherein R' represents independently for each occurrence alkyl.
- 9. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or -OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 10. The trisaccharide of claim 6, wherein said trisaccharide is selected from the group consisting of:

wherein

X is silyloxy or -OC(NH)CCl<sub>3</sub>; and

R is H or silyloxy.

K is it of silyloxy.

A method of preparing a glycosaminoglycan, comprising the step of:

reacting a first mono-, di- or tri-saccharide, comprising an activated anomeric carbon, with a second mono-, di- or tri-saccharide, comprising a hydroxyl or amino group, to form an oligosaccharide, comprising a glycosidic linkage between said anomeric carbon of said first mono-, di- or tri-saccharide and said hydroxyl or amino group of said second mono-, di- or tri-saccharide.

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- The method of claim 11, wherein the first mono-, di- or tri-saccharide is not identical to the second mono-, di- or tri-saccharide.
- The method of claim 11, wherein neither the first mono-, di- or tri-saccharide nor the second mono-, di- or tri-saccharide is covalently linked to a solid support.
- 14. The method of claim 11, wherein the first first mono-, di- or tri-saccharide or the second mono-, di- or tri-saccharide is covalently linked to a solid support.
- 15. The method of claim 14, further comprising the step of:

cleaving said covalent linkage between said oligosaccharide and said solid support with an alkene metathesis catalyst and an alkene.

The method of claim 11, further comprising the step of:

sulfating a hydroxyl or amino moiety of said oligosaccharide.

The method of claim 11, further comprising the step of:

hydrogenolysis. Same as 16, pg: 1340 5tep: (4). 28-29.

A method of preparing an oligosaccharide comprising an  $\alpha$ -glucosamine glycosidic linkage, comprising the step of:

reacting a uronic acid glycopyranosyl acceptor, comprising a hydroxyl group at C4 and a cyclic acetal comprising C1 and C2, with a glycosyl donor, comprising an activated anomeric carbon and an azide functional group at C2, to form an oligosaccharide comprising an α-glycosidic linkage between said hydroxyl group of said uronic acid glycopyranosyl acceptor and said anomeric carbon of said glycosyl donor.

- 19. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is an iduronic acid glycopyranosyl acceptor.
- 20. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is a glucuronic acid glycopyranosyl acceptor.
- 21. The method of claim 18, 19, or 20, wherein said glycosyl donor is a glycosyl fluoride or glycosyl trichloroacetimidate.

22. The method of claim 21, wherein said cyclic acetal comprising C1 and C2 of said uronic acid glycopyranosyl acceptor is an isopropylidene acetal or a cyclopentylidene acetal.

We claim:

1. A disaccharide selected from the group consisting of:

wherein

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or -OC(NH)CCl<sub>3</sub>;

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl.

- 2. The disaccharide of claim 1, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>.
- 3.7 The disaccharide of claim 1, wherein R' represents independently for each occurrence alkyl.
- 4.4 The disaccharide of claim 1, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 5. Pri The disaccharide of claim 1, wherein said disaccharide is selected from the group consisting of:

A trisaccharide selected from the group consisting of:

R'O<sub>2</sub>C

## wherein

X represents independently for each occurrence hydroxyl, acyloxy, silyloxy, halide, alkylthio, arylthio, alkoxy, aryloxy, or -OC(NH)CCl<sub>3</sub>;

R represents independently for each occurrence H, alkyl, aryl, arylalkyl, heteroarylalkyl, silyl, acyl, alkenyloxycarbonyl, or aralkyloxycarbonyl; and

R' represents independently for each occurrence H, alkyl, aryl, arylalkyl, or heteroarylalkyl.

- 7. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>.
- 8. The trisaccharide of claim 6, wherein R' represents independently for each occurrence alkyl.
- 9. The trisaccharide of claim 6, wherein X represents fluoro, bromo, 4-pentenyloxy or OC(NH)CCl<sub>3</sub>; and R' represents independently for each occurrence alkyl.
- 10. The trisaccharide of claim 6, wherein said trisaccharide is selected from the group consisting of:

$$\begin{array}{c} \text{MeO}_2\text{C} & \text{OBn} & \text{AcO} \\ \text{RO} & \text{OBn} & \text{OBn} \\ \text{AcO} & \text{BnO} & \text{OO}_2\text{Me} \\ \text{BnO} & \text{OLev} \end{array} \right; \text{ and}$$

wherein

X is silyloxy or -OC(NH)CCl<sub>3</sub>; and

R is H or silyloxy.

11. A method of preparing a glycosaminoglycan, comprising the step of:

reacting a first mono-, di- or tri-saccharide, comprising an activated anomeric carbon, with a second mono-, di- or tri-saccharide, comprising a hydroxyl or amino group, to form an oligosaccharide, comprising a glycosidic linkage between said anomeric carbon of said first mono-, di- or tri-saccharide and said hydroxyl or amino group of said second mono-, di- or tri-saccharide.

- 12. The method of claim 11, wherein the first mono-, di- or tri-saccharide is not identical to the second mono-, di- or tri-saccharide.
- 13. The method of claim 11, wherein neither the first mono-, di- or tri-saccharide nor the second mono-, di- or tri-saccharide is covalently linked to a solid support.
- 44. The method of claim 11, wherein the first first mono-, di- or tri-saccharide or the second mono-, di- or tri-saccharide is covalently linked to a solid support.
- 15. The method of claim 14, further comprising the step of:

cleaving said covalent linkage between said oligosaccharide and said solid support with an alkene metathesis catalyst and an alkene.

- 16. The method of claim 11, further comprising the step of:
  sulfating a hydroxyl or amino moiety of said oligosaccharide.
- 17. The method of claim 11, further comprising the step of:

removing a hydroxyl or amino protecting group from said oligosaccharide by hydrogenolysis.

18. A method of preparing an oligosaccharide comprising an α-glucosamine glycosidic linkage, comprising the step of:

reacting a uronic acid glycopyranosyl acceptor, comprising a hydroxyl group at C4 and a cyclic acetal comprising C1 and C2, with a glycosyl donor, comprising an activated anomeric carbon and an azide functional group at C2, to form an oligosaccharide comprising an  $\alpha$ -glycosidic linkage between said hydroxyl group of said uronic acid glycopyranosyl acceptor and said anomeric carbon of said glycosyl donor.

- 19. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is an iduronic acid glycopyranosyl acceptor.
- 20. The method of claim 18, wherein said uronic acid glycopyranosyl acceptor is a glucuronic acid glycopyranosyl acceptor.
- 21. The method of claim 18, 19, or 20, wherein said glycosyl donor is a glycosyl fluoride or glycosyl trichloroacetimidate.

22. The method of claim 21, wherein said cyclic acetal comprising C1 and C2 of said uronic acid glycopyranosyl acceptor is an isopropylidene acetal or a cyclopentylidene acetal.